

Laws of thermodynamics and game theory

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Abstract

Using a game theory approach and a new extremal problem, Gibbs formula is proved in a most simple and general way for the classical mechanics case. A corresponding conjecture on the asymptotics of the classical entropy is formulated. For the ordinary quantum mechanics case, the third law of thermodynamics is derived. Some results on the number of ground states and residual entropy are obtained rigorously.

1 Introduction

Let the eigenvalues E_n of the energy operator be given. Consider the mean quantum energy

$$E_q = \sum_n P_n E_n \quad (1.1)$$

and the quantum entropy

$$S_q = - \sum_n P_n \log P_n, \quad (1.2)$$

where P_n are the corresponding probabilities, that is,

$$\sum_n P_n = 1. \quad (1.3)$$

The following statement and definition are well-known.

Second Law of Thermodynamics (see, e.g., [6]). *Let the eigenvalues E_n and mean energy E_q be fixed. Then the entropy S_q takes the maximal value.*

Definition 1.1 (see, e.g., [2]). *Game theory models strategic situations in which an individual's success in making choices depends on the choices of others.*

According to the second law of thermodynamics a problem of the *conditional* extremum appears. Since the extremum is conditional, the connections between the mean energy E_q and entropy S_q can be interpreted in terms of the game theory. We introduce the "compromise" function

$$F = \lambda E_q + S_q, \quad \lambda = -\beta = -1/(kT), \quad (1.4)$$

where k is Boltzmann constant, T is temperature, $\{E_n\}$ and λ are fixed.

Fundamental principle. The function F defines the game between the mean energy E_q and entropy S_q .

In other words, the maximum point $P_{max} = (P_1, P_2, \dots, P_n, \dots)$ of F gives the corresponding probabilities and defines the compromise values of E_q and S_q . We proved in [5] that

$$P_n = e^{\lambda E_n} / Z_q, \quad Z_q = \sum_n e^{\lambda E_n}. \quad (1.5)$$

Thus, we deduced the basic formulas (1.1), (1.2), and (1.5) for the mean energy and entropy (quantum case) using the game theory approach. In the present note we apply the game theory approach to the classical case (Section 2). Section 3 is dedicated to the third law of thermodynamics (classical and quantum cases). For that purpose, we use the results from Introduction and Section 2.

2 Classical thermodynamics and game theory

Let us consider the classical case with the classical Hamiltonian

$$H(p, q) = \frac{1}{2m} \sum_{j=1}^N p_j^2 + V(q), \quad (2.1)$$

where $p = (p_1, p_2, \dots, p_N)$, $q = (q_1, q_2, \dots, q_N)$, p_j are generalized momenta, and q_j are generalized coordinates. The classical mean energy E_c and the classical entropy S_c are defined by the relations

$$E_c = \int \int H(p, q) P(p, q) dp dq, \quad (2.2)$$

$$S_c = - \int \int P(p, q) \log P(p, q) dp dq, \quad (2.3)$$

where

$$P(p, q) \geq 0, \quad \int \int P(p, q) dp dq = 1. \quad (2.4)$$

In the classical case we consider again the game between energy E_c and entropy S_c . The parameter $\beta = 1/kT = -\lambda$ is fixed. In a way, which is quite similar to (1.4), we introduce the compromise function

$$F_c = \lambda E_c + S_c, \quad (2.5)$$

where the parameter $\beta = 1/kT = -\lambda$ is fixed. Next, we use the calculus of variations. The corresponding Euler's equation takes the form

$$\frac{\delta}{\delta P} (\lambda H(p, q) P(p, q) - P(p, q) \log P(p, q) + \mu P(p, q)) = 0. \quad (2.6)$$

Here $\frac{\delta}{\delta P}$ stands for the functional derivation, μ is the Lagrange multiplier, and our extremal problem is conditional (see (2.4)). Because of (2.6) we have

$$\lambda H(p, q) - 1 - \log P(p, q) + \mu = 0. \quad (2.7)$$

From (2.7) we obtain

$$P(p, q) = C e^{\lambda H(p, q)}. \quad (2.8)$$

Formulas (2.4) and (2.8) imply that

$$P(p, q) = e^{\lambda H(p, q)} / Z_c, \quad Z_c = \int \int e^{\lambda H(p, q)} dp dq \quad (2.9)$$

Remark 2.1 *The famous formula (2.9) was deduced above. We think that it was done in the simplest way. Note that*

$$\frac{\delta^2}{\delta P^2} F_c = -1/P < 0. \quad (2.10)$$

It means that, under condition (2.4), the functional F_c of the form (2.5) attains maximum for $P(p, q)$, which is defined by formula (2.9).

3 Third law of thermodynamics

3.1 Quantum case

We suppose that h in the energy operator is fixed and its eigenvalues $E_n = E_n(h)$ are indexed so that

$$E_1 \leq E_2 \leq E_3 \leq \dots \quad (3.1)$$

Similar to (1.5) we assume that the statistical sum Z_q is bounded:

$$Z_q(\beta) = \sum_{n=1}^{\infty} e^{-\beta E_n} < \infty. \quad (3.2)$$

For simplicity, we assume that (3.2) holds for all $\beta > 0$. Since for every $\varepsilon > 0$ there is an N_ε , such that

$$0 < E_n e^{-\varepsilon E_n} < 1 \quad \text{for all } n > N_\varepsilon, \quad (3.3)$$

inequality (3.2) for all $\beta > 0$ implies

$$\sum_{n=1}^{\infty} E_n e^{-\beta E_n} < \infty \quad \text{for all } \beta > 0. \quad (3.4)$$

Therefore, formulas (1.1), (1.4), and (1.5) lead us to the equality

$$E_q(\beta) = \sum_{n=1}^{\infty} E_n e^{-\beta E_n} / Z_q(\beta). \quad (3.5)$$

From (3.2), (3.4), and (3.5) we deduce the following relations:

$$\sum_{n=1}^{\infty} E_n e^{-\beta E_n} = e^{-\beta E_1} (m E_1 + O(e^{-\beta(E_{m+1}-E_1)})), \quad \beta \rightarrow \infty, \quad \beta = 1/kT,$$

$$Z_q(\beta) = e^{-\beta E_1} (m + O(e^{-\beta(E_{m+1}-E_1)})), \quad \beta \rightarrow \infty, \quad \beta = 1/kT, \quad (3.6)$$

$$E_q(\beta) = E_1 + O(e^{-\beta(E_{m+1}-E_1)}), \quad \beta \rightarrow \infty, \quad \beta = 1/kT, \quad (3.7)$$

where m is the multiplicity of E_1 .

Equalities (1.2), (1.4), and (1.5) imply a formula for entropy

$$S_q(\beta) = \beta E_q(\beta) + \log Z_q(\beta). \quad (3.8)$$

Using relations (3.6)-(3.8) we obtain

$$S_q(\beta) \rightarrow \log(m), \quad \beta \rightarrow \infty, \quad \beta = 1/kT. \quad (3.9)$$

Compare (3.9) with the well-known statement:

Third law of thermodynamics. If $\beta \rightarrow \infty$, then $S_q(\beta) \rightarrow 0$.

Thus, we proved the following assertion.

Theorem 3.1 *Let the conditions (3.1) and (3.2) be fulfilled. Then the relation $m = 1$ and the third law of thermodynamics are equivalent.*

Remark 3.2 *The equality $m = 1$ means that the ground state is non-degenerate.*

Remark 3.3 *If $m > 1$ we obtain the so called residual entropy $\log(m)$ (see [1]).*

3.2 Classical case

Now, we consider briefly the third law of thermodynamics for the classical case. First, assume that the dimension N of the coordinate space equals 1. In case of a potential well the following formulas:

$$E_c(\beta) = 1/(2\beta), \quad Z_c(\beta) = \sqrt{2\pi m a^2 / \beta} \quad (3.10)$$

hold (see [3, 4]). The corresponding formulas for the oscillator (see [3]) have the form

$$E_c(\beta) = 1/\beta, \quad Z_c(\beta) = 2\pi/(\beta\omega). \quad (3.11)$$

It follows from (2.2), (2.3), and (2.9) that

$$S_c(\beta) = \beta E_c(\beta) + \log Z_c(\beta) \quad (3.12)$$

Because of (3.12), in both cases (3.10) and (3.11) we have

$$S_c(\beta) = c_1 + c_2 \log \beta, \quad (3.13)$$

where c_1 and c_2 are constants. Note that relation (3.13) holds also for an arbitrary N (the corresponding formulas for the potential well are adduced in [5]). In view of (3.13), we formulate our conjecture:

Conjecture 1. In the classical case the following result

$$S_c(\beta) = c_1 + c_2 \log \beta + o(1), \quad \beta \rightarrow \infty$$

is valid.

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